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WASTE SURVEY REPORT. BUFFALO REFINERY, SOCONY MOBILE OIL COMPANY, BUFFALO, NEW YORK

PUBLIC HEALTH SERVICE
BUFFALO, NEW YORK

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WASTE SURVEY REPORT

BUFFALO REFINERY

SOCONY MOBIL OIL COMPANY

BUFFALO, NEW YORK

Prepared by

H. A. Anderson, Public Health Engineer

I. J. C. Field Unit, USPHS

Buffalo, New York

Date of Survey

July 15 to July 20, 1956.

Purpose

This survey was conducted to obtain information on the current quantity of wastes in the refinery effluent pertinent to water pollution problems of the International Boundary Waters in the Niagara River area. It is part of the continuing water pollution abatement program being conducted by the New York Water Pollution Control Board in the endeavor to achieve the Objectives for Boundary Water Control Adopted by the International Joint Commission.

Personnel Participating

SOCONY MOBIL OIL COMPANY

Carl Dubois, Technical Director

C. F. Brandt, Chief Chemist

J. H. Twist, Control Chemist

W. F. Walsh, Group Leader, Physical Testing

Don Gleason, Process Engineer

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16. Abstracts The current quantity of wastes in refinery effluent pertinent to water pollution problems of the Niagara River area is investigated as a part of the water pollution abatement program by the N. Y. Water Pollution Control Board. Wastes from the refinery are segregated and discharged to the Buffalo River through three oil separators. Chlorides and sediment-oil water emulsion in the crude oil are removed by injecting a caustic demulsifier and treated water into the crude oil, preheating, and settling. Water containing 4 to 5 ppm of oil is rejected to waste. Data indicates a significant reduction in quantity of oil discharged; however, oil films on the river indicate greater than desireable quantities of oil continue to enter the river from some source.

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Personnel Participating, continued

PUBLIC HEALTH SERVICE

H. A. Anderson, Public Health Engineer

M. W. Ruszaj, Chemist

W. C. Culliton, Aide

Organization of Survey

This survey was cooperatively conducted by the Socony Mobil Oil Company and the I. J. C. Field Unit of the Public Health Service. Specific arrangements for the study were made at the conference of Socony Mobil Technical Personnel and the I. J. C. Field Unit Staff on July 10, 1956.

The Socony Mobil Oil Company agreed to collect composite samples of the intake water, Thermofor Catalytic Cracking (TCC) Unit Separator effluent, Main Oil Trap or Separator effluent and the No.2 Reformer Oil Separator effluent. It was determined that one 24 hour sample of the reformer effluent would be sufficient inasmuch as the reformer was soon to be permanently taken out of production and previous data had indicated that this effluent contributed a relatively small portion of the refinery waste load.

Similar samples were to be provided the refinery and I. J. C. Field Unit Laboratories. The I. J. C. Field Unit was to determine the oil, phenol, chlorine demand, solids, and cyanide content and such other characteristics as the alkalinity, acidity and pH of the refinery intake and effluents. Although short staffed due to vacation, the refinery laboratory was to make some oil, sulfide, and mercapten determinations and others if possible.

GENERAL INFORMATION

Refining Operations

This oil refinery accomplishes the separation and purification of a mixed

base crude, 36 to 38 gravity, received from the Illinois, Oklahoma, and East and West Texas Fields by pipe line. Processing equipment includes single and two stage distillation units for crude fractionation, a catalytic cracking unit, stabilizers or pressurized fractionating towers, caustic soda scrubbers and a copper sweetening unit for mercaptan removal together with various other stills and equipment for product separation and purification. The thermal reforming unit in operation during the study was replaced with a catalytic reformer about the middle of August, 1956. It is believed that this change will not materially affect quantity of water pollution substances in the refinery wastes.

The principal products of the refinery are motor gasoline, kerosene, light and heavy residual fuel oils, refined wax, light viscosity lubricating oils and asphalt. Except for periodic shut-downs of various units for inspection, general maintenance and repair, the refinery operations are on a continuous 24 hour day 7 day week basis.

Capacity and Operating Rate

The crude oil input of 25,000 barrels (42-gallon barrels) per day during this survey closely approached the maximum refinery capacity of 26,000 barrels. During the study the total feed to the catalytic cracker was 15,400 barrels per day, of which 11,600 barrels was fresh feed.

A new crude distillation unit is expected to be completed in 1958 which will increase the refining capacity to 28,500 barrels of crude oil input per day.

Employees

The total number of employees at the refinery including office personnel, is approximately 400.

Water Supply

City of Buffalo water is purchased for drinking and sanitary purposes; and to very limited extent, for steam make-up and other process water. Cooling water is obtained from the Buffalo River through two submerged shore intakes at the south edge of the refinery property. Both intakes are less than 400 feet upstream from two process effluent sewers, and a short distance downstream from the No.2 reformer effluent sewer. At times there is either negligible or upstream flow in the river at this point, during which there is considerable recycling of the refinery effluent. The river water is measured with orifice meters and the city water purchased is measured with positive displacement meters.

PROCESS WASTES

Wastes from the refinery are segregated and discharged to the Buffalo River through three oil separators designated as follows:

A. Thermofor catalytic cracking (T.C.C.) unit separator

B. No.2 reformer separator

C. Master separator

T.C.C. Separator

The influent of the T.C.C. separator consists solely of river water used for indirect cooling in the catalytic cracking unit. The separator is one compartment or section of the master separator. At the effluent flow of 4.48 MGD obtained in this study and assuming a water depth of 9.5 ft., the theoretical detention period in the separator is approximately 52 minutes. Sediment deposits in the separator significantly reduce this detention period. The purpose of this separator is to catch any oil losses which might occur in the event of leakage or failure of the indirect cooling units. Separated water is discharged directly to

the Buffalo River.

No.2 Reformer Separator

River water used for cooling of the gasoline streams from the reformer unit are discharged into this separator. Surface water with any floating oil present is being continuously skimmed and sent to the master separator. The purpose of this separator is to prevent oil losses due to condenser failure and reduce the volumetric load on the master separator. Separated water is discharged to the Buffalo River.

Master Separator

All process wastes other than the above are discharged to the master separator. Waste from the lube oil treating and wax production departments pass through departmental separators equipped with skimming devices before discharge to the master separator. At the rate of flow determined in this study, the theoretical detention period in this separator is approximately 2-3/4 hours. Actual detention is appreciably reduced by sediment deposits which are removed biannually or even less frequently.

Floating oil and emulsion is skimmed from all compartments of the separator daily, and transferred to tanks and heated to a temperature of about 180° F. to break emulsions and improve separation. Persistent oil emulsions not responding to this treatment can be transferred to an agitator where somewhat higher temperatures and chemical demulsifiers are employed. Recovered oils, averaging approximately 800 barrels per day, are reprocessed and separated water is returned to the master separator.

Separated water from the master separator is discharged to the Buffalo River through 2 submerged outlet pipes.

Other Waste Control Measures

Salts (chlorides) and sediment-oil water emulsion in the crude oil as received is removed by injecting caustic, a patented demulsifier, and treated water (5% crude) into the crude, preheating and settling. Water containing only 4 to 5 ppm of oil is rejected to waste.

Sludges formed in the acid treating of lubricating oils are burned.

The emulsion (white water) formed during caustic neutralization following acid treatment of lube oils is broken by neutralization with calcium chloride and agitation and settling. It is reported that the waste water from this process contains relatively little oil.

Cresylates are separated from spent caustic treating wastes by treating these wastes with recovered hydrogen sulfide originally present in the crude or formed in the cracking process. The cresylates (phenolic materials) are sold as raw cresylic acid. The sodium sulfide which is also formed in this process is recovered and sold as a crude grade of sodium sulfide. Mercaptans and excess hydrogen sulfide are collected and burned with excess refinery gas at the flare stack.

SURVEY METHODS

Flow Measurements

Because of the inaccessibility of the effluent sewers flow velocity measurements were made with a Price Current Meter in the single inlet pipe to the T.C.C. separator and the three inlet pipes to the master separator. Velocity measurements were made at a number of points in a plane perpendicular to the longitudinal axis of the pipe, the data plotted to scale and the flow calculated by multiplying the average velocity determined in various sectors of the pipe by the area of the respective sectors. The discharge of the No.2 reformer separator was

determined at the effluent weir by measuring the head of water over the weir.

Flow measurements were attempted on July 16 and 23. Measurements obtained July 16 were unsatisfactory and therefore discarded. Satisfactory measurements were obtained on July 23.

The measured total effluent flow was approximately 4.0 per cent less than the total volume of process intake water on July 23, which is a satisfactory check.

Use of the July 23 effluent flow measurements in calculations of this report is justified on the basis that the volume of process intake water during the study was approximately the same as that of July 23.

Sampling

Samples were collected every three hours and composited over the 24 hour period from 8:00 A.M. to 8:00 A.M. Samples of phenol analyses were preserved with $CuSO_4$, and the samples for cyanide determinations were preserved by adding sufficient NaOH to provide a pH of 11 or above. Samples for cyanide analyses were collected on only one day of the survey as it was believed that the waste did not contain significant quantities of cyanide, which proved to be true. For the oil determination a 4 oz. sample was collected every 3 hours and poured into a glass-stoppered one liter bottle.

Analytical Methods

Analysis for cyanide, oil, phenol, and pH were made by the methods adopted as Official Methods for Boundary Water Quality by the Board of Technical Advisers to the International Joint Commission. Acidity, alkalinity, chlorine demand and solids determination were made according to procedures given in "Standard Methods for the Examination of Water, Sewage, and Industrial Wastes," published by the American Public Health Association.

The chlorine demand determination was based on a 15 minute contact period with a total combined and free available chlorine residual of 0.5 ppm. Residuals were measured by the Orthotolidine Colormetric Method.

The mercaptan and sulfide determination were made by the Socony Mobil Laboratory using the Shell Electrometric Titration Method.

RESULTS

The results of the waste determinations are presented in Tables 1 through V.

The analytical results reported are those of the I.J.C. Field Unit Laboratory with the exception of the mercaptan and sulfide data which were furnished by the Socony Mobil Laboratory. Oil determinations made by both laboratories were in substantial agreement.

A comparison of the net oil, phenol, solids and chlorine demand discharged to the Buffalo River during this survey with 1949 and 1952 studies made by the Socony Mobil Oil Company are presented in Table VI. Although a small portion of the intake water eventually discharged as effluent from the main separator was Buffalo City water it was assumed for the purpose of calculating the net waste load discharged that all of the process water was Buffalo River water. The error of this assumption is within the limits of accuracy of the waste discharge determinations.

The data in Table VI shows that there has been a significant reduction in the net oil discharge during this survey as compared with the 1952 study made by the Socony Mobil Company. There was relatively little change in the net phenol and suspended solids discharged, but some increase in the total solids and chlorine demand in the waste.

CONCLUSION

It is concluded that this Socony Mobil Refinery is generally accomplishing good control of process waste losses. The increase in the net total solids and chlorine demand presently discharged as compared to 1952 is not believed to significantly affect the quality of Buffalo River or Boundary Waters.

It is concluded that the data indicates a very significant reduction in the quantity of oil discharged, which should have a very beneficial effect on the quality of Buffalo River water. In spite of this reduction, observations of oil films on the river indicate that greater quantities of oil than desirable continue to enter the river from some source.

TABLE I

ANALYSIS OF OIL AND PHENOL CONTENT
OF INTAKE WATER AND EFFLUENTS

SOURCE	DATE 1956	FLOW MGD	OIL GROSS PPM	OIL NET PPM	OIL NET DISCHARGE lbs./day	PHENOL GROSS PPB	PHENOL NET PPB	PHENOL NET DISCHARGE lbs./day
BUFFALO RIVER	7/16		7.9			45		
	7/17		10.5			48		
	7/18		1.5			57		
	7/19		3.3			17		
	7/20		4.4			54		
	Average		5.5			44.2		
EFFLUENT TCC	7/16	4.48	2.0	-5.9	-220	23	-22	-.82
	7/17	4.48	7.3	-3.2	-120	21	-27	-1.01
	7/18	4.48	2.0	0.5	19	0	-57	-2.13
	7/19	4.48	2.7	-0.6	22	17	0	0
	7/20	4.48	18.2	13.8	516	39	-15	-.56
	Average	4.48	6.4	0.9	34	20	-24	-.9
EFFLUENT MAIN TRAP	7/16	13.66	15.2	7.3	831	2352	2307	263
	7/17	13.66	13.6	3.1	353	2368	2320	264
	7/18	13.66	14.2	12.7	1447	2252	2195	250
	7/19	13.66	7.0	3.7	421	1972	1955	223
	7/20	13.66	3.5	-0.9	-103	1472	1418	162
	Average	13.66	10.7	5.2	590	2083	2039	232
EFFLUENT NO. 2 REFORMER	7/20	3.62	6.7	2.3	69	38	-16	-0.48

TABLE II

ANALYSIS OF CHLORINE DEMAND OF
INTAKE WATER AND EFFLUENTS

SOURCE	DATE 1956	FLOW MGD	CHLORINE DEMAND GROSS PPM	CHLORINE DEMAND NET PPM	CHLORINE DEMAND NET DISCHARGE lbs./day
INTAKE BUFFALO RIVER	7/16		2.06		
	7/19		1.50		
	7/20		1.58		
	Average		1.71		
EFFLUENT TCC	7/20	4.48	1.42	-0.16	-5.98
EFFLUENT MAIN TRAP	7/16	13.66	3.50	1.44	164
	7/19	13.66	8.30	6.80	775
	7/20	13.66	5.10	3.52	401
	Average	13.66	5.63	3.92	446
EFFLUENT NO. 2 REFORMER	7/20	3.62	1.78	0.20	6.03

TABLE III

ANALYSIS OF SOLIDS CONTENT OF
INTAKE WATER AND EFFLUENTS

SOURCE	DATE 1956	FLOW MGD	SUSPENDED SOLIDS			TOTAL SOLIDS		
			GROSS ppm	NET ppm	NET DISCHARGE lbs./day	GROSS ppm	NET ppm	NET DISCHARGE lbs./day
INTAKE	7/16		61			331		
BUFFALO	7/17		43			330		
RIVER	7/18		26			278		
	7/19		20			344		
	7/20		29			285		
	Average		35.8			313.6		
EFFLUENT	7/16	4.48	85	24	897	345	14	523
TCC	7/17	4.48	46	3	112	320	-10	-374
	7/18	4.48	34	8	299	243	-35	-1308
	7/19	4.48	24	4	150	316	-28	-1046
	7/20	4.48	28	-1	-37	318	33	1233
	Average	4.48	43	8	284	308	-5	-194
EFFLUENT	7/16	13.66	50	-11	-1253	403	72	8201
MAIN	7/17	13.66	60	17	1936	373	43	4898
TRAP	7/18	13.66	44	18	2050	442	164	18680
	7/19	13.66	49	29	3303	426	82	9340
	7/20	13.66	44	15	1708	357	72	8201
	Average	13.66	49	14	1549	400	87	9864
EFFLUENT NO. 2 REFORMER	7/20	3.62	33	4	120	379	94	2828

TABLE IV

ACIDITY, ALKALINITY, pH, MERCAPTANS AND SULFIDES
ANALYSES OF INTAKE WATER AND EFFLUENTS

SOURCE	DATE 1956	FLOW MGD	ACIDITY ppm	ALKALINITY ppm	pH	MERCAPTANS	SULFIDES
INTAKE	7/16		14	110	6.9	Nil	Nil
BUFFALO	7/17		24	124	7.1	Nil	Nil
RIVER	7/18		16	100	7.2	Nil	Nil
	7/19		8	88	6.8	Nil	Nil
	7/20		24	112	6.5	Nil	Nil
	Average		17	107	6.9	Nil	Nil
EFFLUENT	7/16	4.48	15	104	6.8	Nil	Nil
TCC	7/17	4.48	28	118	7.3	Nil	Nil
	7/18	4.48	14	114	7.4	Nil	Nil
	7/19	4.48	14	120	6.9	Nil	Nil
	7/20	4.48	40	116	6.9	Nil	Nil
	Average	4.48	22	114	7.1	Nil	Nil
EFFLUENT	7/16	13.66	14	110	6.9	Nil	Nil
MAIN	7/17	13.66	30	118	7.2	Nil	Nil
TRAP	7/18	13.66	26	108	6.9	Nil	Nil
	7/19	13.66	16	120	6.9	Nil	Nil
	7/20	13.66	24	112	6.5	Nil	Nil
	Average	13.66	22	114	6.9	Nil	Nil
EFFLUENT NO. 2 REFORMER	7/20	3.62	20	112	6.6	Nil	Nil

TABLE V

SUMMARY OF NET WASTE LOAD ON BUFFALO RIVER

SOURCE	OIL		PHENOL		SUSPENDED SOLIDS		TOTAL SOLIDS		CHLORINE DEMAND	
	lbs/day	lbs.per 1000 bbls. oil input	lbs/day	lbs.per 1000 bbls. oil input	lbs/day	lbs.per 1000 bbls. oil proc.	lbs/day	lbs.per 1000 bbls. oil proc.	lbs/day	lbs.per 1000 bbls. oil proc.
T.C.C.	34	1.4	-1	.0	284	11.3	-194	-7.8	-6	-0.2
MAIN TRAP	590	23.6	232	9.3	1549	62.0	9864	394	446	17.8
#2 REFORMER	7	.3	0	0	120	4.8	2828	113	6	0.2
TOTAL	631	25.3	231	9.3	1953	78.1	12498	499	446	17.8

TABLE VI

COMPARISON OF NET WASTE LOAD IN POUNDS PER DAY WITH RESULTS OF PREVIOUS STUDIES

	OIL			PHENOL			SUSPENDED SOLIDS			TOTAL SOLIDS			Cl. DEMAND		
SOURCE	1949	1952	1956	1949	1952	1956	1949	1952	1956	1949	1952	1956	1949	1952	1956
T.C.C.	946*	-15	34	1.5*	2.3	-1	-1274*	220	284	407*	150	-194	39*	33	-6
MAIN TRAP	675	3338	590	89.6	205.0	232	460	2230	1549	9900	8000	9864	119	93	446
#2 REFORMER	-	-30	7	-	-0.2	0	-	-179	120	-	-370	2828	-	3	6
TOTAL	1621	3293	631	91.1	207.1	231	-814	2271	1953	10307	7780	12498	158	129	446

* HOUDRY GASOLINE CRACKING UNIT